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Published in:
Journal of Supercritical Fluids

DOI:
[10.1016/j.supflu.2008.08.011](https://doi.org/10.1016/j.supflu.2008.08.011)

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Document Version
Publisher's PDF, also known as Version of record

Publication date:
2008

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Citation for published version (APA):

Leusbrock, I., Metz, S. J., Rexwinkel, G., & Versteeg, G. F. (2008). Quantitative approaches for the description of solubilities of inorganic compounds in near-critical and supercritical water. *Journal of Supercritical Fluids*, 47(2), 117-127. <https://doi.org/10.1016/j.supflu.2008.08.011>

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Quantitative approaches for the description of solubilities of inorganic compounds in near-critical and supercritical water

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ARTICLE INFO

Article history:

Received 24 April 2008

Received in revised form 24 July 2008

Accepted 11 August 2008

Keywords:

Supercritical water

Salt

Solubility

Phase equilibrium

ABSTRACT

The decreased solubility of salts in supercritical water is of great interest for industrial applications and scientific work.

Several methods to quantify this decreased solubility are described and reviewed by applying them on experimental solubility data. The salts used for comparison are NaCl, NaNO₃, Na₂CO₃, Na₂SO₄, PbO and CuO. The approaches used for comparison are of semi-empirical and empirical origin. Resulting from this comparison, one approach based upon the description of the phase equilibrium between the solid salt phase and the supercritical water phase is chosen as the most appropriate one. Additionally, parameters for the description of the solubilities of NaCl, NaNO₃, Na₂CO₃, Na₂SO₄, PbO and CuO with this approach at supercritical conditions are presented.

To extend the known solubility data of salts an experimental setup was designed which uses a continuous feed stream with a known concentration. This stream is pressurized and heated to the temperature and pressure of interest. Due to the elevated temperatures and pressures, a supersaturation occurs and precipitation takes place. The solubility of NaCl in the range of 380–410 °C and 170–235 bar is determined with this method. The experimental results agree well with other studies which investigated the solubility of NaCl and extend the known solubility data to higher densities.

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1. Introduction

Supercritical fluids have received an increasing attention in literature and research over the last decades. While the usage of supercritical carbon dioxide for industrial applications is well established (particle formation, extraction, drying), the application of supercritical water is still mostly in the developing stage or entering the pilot plant stage. With the growing number of possible processes for supercritical water like SCWO¹ [1–5], reactions in near critical and supercritical water [6–8], particle formation [9–11] as well as gasification of biomass in supercritical water [12,13], an urgent need exists for consistent methods and approaches to understand and describe these systems.

Due to the changing properties of water at supercritical conditions and the change in solvation behavior of water from a polar to a non-polar medium, inorganic compounds and salts and the corresponding precipitates are considered as new challenging options

for applications with supercritical water. In order to be able to evaluate the feasibility, both technically and economically, respectively, of the precipitation of e.g. salts in supercritical water, it is required to have a good thermodynamically correct description of these phenomena. Unfortunately, the precise and easily accessible description of the solubility of a salt–water system or more complex electrolyte systems at elevated temperatures and pressures – which is inevitable to develop and design industrial applications – is not readily available.

Information at ambient conditions, due to a long history of research and applications, is well established; the same is not valid for systems at a supercritical state. Here the existing data and approaches lack the width and validation, compared to the data available for ambient conditions.

Several approaches exist in open literature dealing with the description of solubilities of salts in supercritical water with differing degrees of complexity and thermodynamical background. No consensus exists in literature and research which type of model is the most suitable for the description of the solubility.

The aim of this work is to present an overview of the methods that are available for the description of solubilities of salts in supercritical water. This work wants to compare these methods with each

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¹ Supercritical Water Oxidation.

Nomenclature

Roman letters

A, B, C	fitting parameters in Eq. (15)
A', B', C', D'	fitting parameters in Eq. (16)
c	concentration, molality (mol/L, mol/kg)
$d \dots k$	fitting parameters in Eqs. (1) and (2)
G	Gibbs enthalpy (kJ/kg, kJ/mol)
H	enthalpy (kJ/kg, kJ/mol)
K_a	association equilibrium constant
K_s, K_s^*	phase equilibrium constant
R	universal gas constants (J/mol K)
S	entropy (kJ/kg K, kJ/mol K)
T	temperature (K)
v	molar volume (L/mol)
y	molar fraction

Greek letters

α	activity (mol/kg)
δ	solubility parameter
ρ	density, molar density (mol/L, kg/m ³)

Indices

a, b	counter for the number of cations/anions in a salt
c, d	valency of the cation/anion
f	fluid
MeX	referring to the salt of interest, Me corresponds to the cation, X to the anion
s	solid

Superscripts

i, j, k, l	fitting parameters for Eqs. (1) and (2)
m	melting property
n	hydration number
0	reference state

other in order to correlate experimental results. As a result of this comparison, one method is chosen as the most appropriate one for a simple description of solubility in supercritical water. Additionally, one objective of this paper is to investigate the solubility of several salts in near-critical and supercritical water and to supply parameters for the description of their solubility.

To increase the amount of available property data, an experimental setup for the measurement of solubilities is presented here as well as experimental results of sodium chloride in near-critical and supercritical water in the temperature range of 380–410 °C and 170–235 bar.

2. Theoretical background

Two relevant methods for the description of the solubility of a salt–water system can be taken into consideration. *Equations of state*² can be used as well as *empirical and semi-empirical* approaches. Both methods have different levels of complexity and areas of application. While the equations of state provide system properties like activity coefficients and enthalpy, they require a sound knowledge of the thermodynamic background in order to develop a generally applicable tool. Empirical and semi-empirical approaches provide the desired property data while an exact thermodynamic description of the system is not necessarily given.

Approaches using molecular dynamics have shown interesting insights in the fundamental ideas of supercritical water and systems containing supercritical water and inorganic compounds [14–18]. These studies are focused on the behavior of supercritical water and not on the quantitative description of the solubility of salts. Therefore, these results are not included here. Yet the application of molecular dynamics is a powerful tool to understand the basic phenomena occurring in supercritical water.

The focus of this paper is put on the application of empirical and semi-empirical approaches for the description of the solubility due to their simplicity and their straight-forward character. Nevertheless, the application of an EOS can be the tool of choice for more complex problems (e.g. mixtures, description of precipitation processes, transport phenomena and reactions [19,20,10,21]).

2.1. Equations of state

One of the most frequently applied equations of state model for electrolyte solutions is based on the works of Pitzer [22–24]. This model was applied successfully on multi-electrolyte systems and used to describe systems in subcritical and supercritical state [25–27]. The equation itself consists of two parts. The first part is the reference part in which all the properties of a mixture of hard-sphere ion pairs – resembling the salt–water matrix – are calculated. The second part, the perturbation part, represents all other interactions and is expressed by a virial-type function. The large amount of parameters in this type of model are fitted to the experimental data available. Binary and ternary systems like e.g. NaCl–H₂O and KCl–NaCl–H₂O were described with good accuracy [25–27]. Furthermore, extensions to systems including organic substances have been published [28–31]. To improve on the predictive quality of the EOS for systems where little experimental data is available, Kosinski and Anderko [32] introduced a three-parameter corresponding state approach together with a predictive procedure based on the reference system NaCl–H₂O. Liu et al. [33] further included dissociation effects of NaCl in an extension of the Pitzer-EOS which are known to occur in supercritical electrolyte systems and were only included implicitly in the perturbation term of the original Pitzer-EOS. Additionally, experimental data on the heat of dilution and the apparent molar volume of NaCl was used by Liu et al. [33] to improve on the quality of the correlation parameters.

A second equation of state that was developed for the description of salt–water systems is based on the work of Helgeson and Kirkham [34–36] and of Shock and Helgeson [37–40], respectively. Here any molal thermodynamic property is considered to be a sum of intrinsic and electrostatic effects. The intrinsic contributions are related to the properties of the ion while the electrostatic contributions result must be plural from the interaction of ion and water which is described by an effective electrostatic radius of the ion as a function of the system state. The advantage of this equation of state is that the behavior of systems can be predicted from standard state properties, where no or only little experimental data is available. The development of this equation of state has lead to a free accessible computer program called SUPCRT92 for the description of different electrolyte systems at elevated pressures and temperatures [41].

The advantages of the usage of equations of state is quite obvious. Next to the desired solubility data, it is also possible to gain information on additional thermodynamic property like enthalpy or molar volume. This additional information can lead to a better understanding of the system behavior. Another positive aspect is the adaptability to specific problems and the possibility to extend the equation of state to multi-component mixtures and to organic substances. Nevertheless the equations of state represent a rather

² In the following abbreviated with EOS.

complex tool for the description of a system. Changes or extensions are difficult without a sound and extended background knowledge as well as time consuming.

2.2. Empirical and semi-empirical approaches

Empirical and semi-empirical approaches are based on correlations between solubility and the system parameters temperature, pressure and density resulting from regression of experimental data over the system parameters. These correlations can be used for quick yet precise calculations of the solubilities as well as for design purposes for industrial setups. Next to that, the correlations are usually far less complex than an equation of state. This can be also regarded as a drawback since e.g. an extension to mixtures is not possible without major changes. An exact thermodynamical representation of the system is not necessarily given due to the assumptions commonly made in these approaches. Also predictions beyond the range of experimental data used in the correlation have to be treated carefully.

The simplest method to describe the solubility empirically is to express the solubility as a polynomial function of one of the system parameters, preferably the density. This approach lacks any thermodynamical background yet an accurate representation of the solubility can be achieved in the range of the experimental data used for the correlation [42,43].

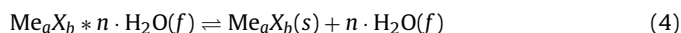
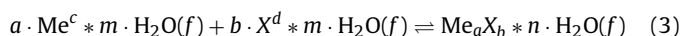
$$c_{MeX} = d \cdot \rho^i \quad (1)$$

$$\log c_{MeX} = e \cdot \rho^j + f \cdot \rho^k + \dots + g \cdot \rho^l + h \quad (2)$$

Me represents the salt cation, X the salt anion, ρ the density of the pure solvent; d, e, f, g, h, i, j, k and l are fitting parameters.

Most semi-empirical approaches are based on a derivation of standard phase equilibrium thermodynamics [44–47]. Investigating a salt concentration–solvent density diagram two different phases/phase compositions can be distinguished (cp. Fig. 1). Below the solubility curve only a single supercritical fluid phase with complexes of associated salt ion pairs and water; above the solubility curve a supercritical water phase and a solid salt phase can be found [48].

Right on the solubility curve of a salt a phase equilibrium exists that can be interpreted for a single salt–water system as followed:



Me represents the salt cation while X represent the salt anion; a and b are the number of ions in the salt molecule, c and d its valency.

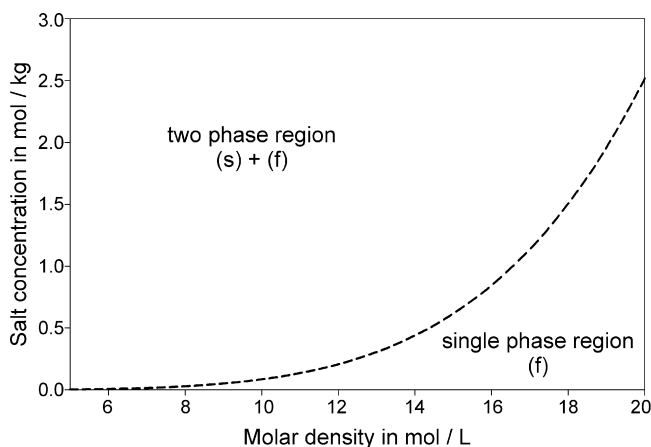


Fig. 1. Solubility curve of NaCl.

n, m and p is the number of water molecules needed for solvation for the salt and the ions while s and f refer to the phases solid and fluid. Regarding the equilibrium, it is assumed that the formation of a solid only takes place via the associated complex and not via the dissociated salt ions.

The definition for the phase equilibrium constant for this transition results in the following:

$$K_s = \frac{\alpha_{Me_aX_b * n \cdot H_2O(f)}}{\alpha_{Me_aX_b(s)} \cdot \alpha_{H_2O(f)}^n} \quad (5)$$

α refers to the activity coefficient of the species on a molality base.

In order to simplify this equation several assumptions can be made. First of all, the activity coefficient of the solid salt is regarded as unity. Also the interaction of the solvated salt complex as well as of the water molecules is neglected. The fluid phase is interpreted as an ideal one. Concluding from that the activity coefficient of the salt complex now represents the concentration of the salt complex while the activity coefficient of water is approximated as the density of the pure solvent [45,44]. With the density of the solvent as a function of temperature and pressure being the parameter of choice to describe the state of the system, also the change in solvation behavior is included in this approach. Water changes from a polar solvent at ambient state to a non-polar one at supercritical conditions. This change can be described by the change of the dielectric constant. The dielectric constant is a relative measure of the polarity of a solvent and is a function of the temperature and the pressure, therefore of the density. For water, the dielectric constant changes from around 80 at ambient to below 5 for $p = 25$ MPa and $T \geq T_c$ (cp. Fig. 2).

A description of these parameters on a molar base is chosen. The concentrations are treated as molalities. The density of water is used on a molar base resulting in the density resembling a concentration of water molecules per volume unit.

$$K_s^* \approx \frac{c_{Me_aX_b * n \cdot H_2O(f)}}{1 \cdot \rho_{H_2O(f)}^n} \quad (6)$$

$$\Rightarrow c_{Me_aX_b * n \cdot H_2O(f)} = K_s^* \cdot \rho_{H_2O(f)}^n \quad (7)$$

The equilibrium constant K_s^* can be interpreted with a standard Arrhenius approach.

$$K_s^* = \exp \left(- \frac{\Delta G_{solv}}{R \cdot T} \right) \quad (8)$$

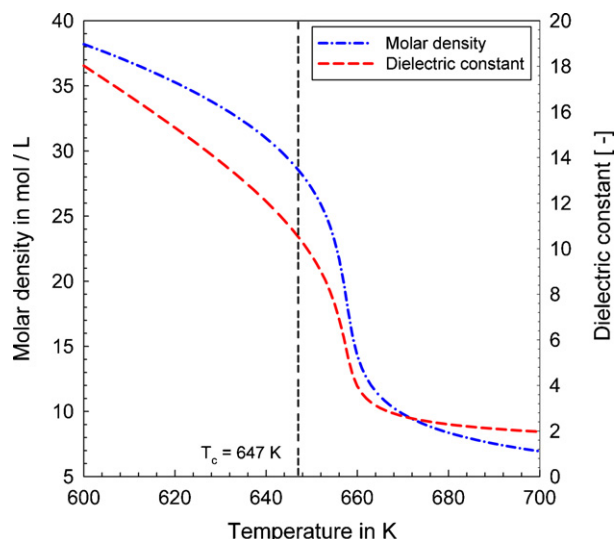


Fig. 2. Comparison of molar density and dielectric constant at 25 MPa [62].

$$= \exp \left(-\frac{\Delta H_{\text{solv}}}{R \cdot T} + \frac{\Delta S_{\text{solv}}}{R} \right) \quad (9)$$

$$\Rightarrow \log c_{\text{MeX}, \text{H}_2\text{O}} = \log K_s^* + n \cdot \log \rho_{\text{H}_2\text{O}} \quad (10)$$

$$= -\frac{\Delta H_{\text{solv}}}{R \cdot T} + \frac{\Delta S_{\text{solv}}}{R} + n \cdot \log \rho_{\text{H}_2\text{O}} \quad (11)$$

R is the universal gas constant, T the system temperature. For the Gibbs enthalpy of solvation, ΔG_{solv} , the heat of solvation, ΔH_{solv} , and the entropy of solvation, ΔS_{solv} , it is assumed that they are independent of the system parameters temperature, pressure and density.

Another approach based on the description of the phase equilibrium is also possible while choosing another expression for the equilibrium constant [47].

$$\Delta G = -R \cdot T \cdot \ln K_s^* \quad (12)$$

$$\Delta G(T) = \Delta H(T) + \Delta S(T) \cdot T \quad (13)$$

$$= \Delta H^0 - T \cdot \Delta S^0 + \int \Delta c_p dT - T \int \frac{\Delta c_p}{T} dT \quad (14)$$

$$= A - \frac{B}{T} - C \cdot T \ln T \quad (15)$$

Eq. (15) combined with Eqs. (7) and (12) leads to following expression for the solubility:

$$\ln c_{\text{MeX}} = A' - \frac{B'}{T} + C' \ln T + D' \ln \rho \quad (16)$$

A, B, C, A', B', C' and D' are fitting parameters, c_p represents the isothermal heat capacity, the superscript 0 the reference state.

2.3. Further approaches

Additional to the approaches already mentioned, other methods which were successfully applied on systems at ambient state were investigated for the usage on a supercritical or near critical salt–water system [49,50,3]. The Flory-Huggins theory, frequently used for the description of organic systems, was adapted for the usage in a supercritical system and applied for the modeling of supercritical carbon dioxide and water systems [51]. In combination with regular solution theory a model was derived to interpret the solubility as mole fraction y in a convenient way.

$$\ln y_{\text{MeX}} = \frac{\Delta h_{\text{MeX}}^m}{R \cdot T} \left(\frac{T}{T_{\text{MeX}}^m} - 1 \right) - \frac{v_{\text{MeX}}}{R \cdot T} (\delta_{\text{H}_2\text{O}} - \delta_{\text{MeX}})^2 - 1 + \frac{v_{\text{MeX}}}{v_{\text{H}_2\text{O}}} - \ln \frac{v_{\text{MeX}}}{v_{\text{H}_2\text{O}}} \quad (17)$$

For this approach it is assumed that the supercritical phase behaves as an expanded liquid and the liquid phase does not dissolve in the solid phase. Here the properties of the salt, especially the melting temperature ΔT_{MeX}^m and the heat of melting Δh_{MeX}^m , are used next to the properties of a pure water system to describe the salt–water system. v_i and δ_i denote the molar volume of the species as well as the solubility parameter [49].

3. Experimental

3.1. Experimental setup

In order to measure the solubilities of the salts in water at supercritical and near critical conditions, an experimental setup was

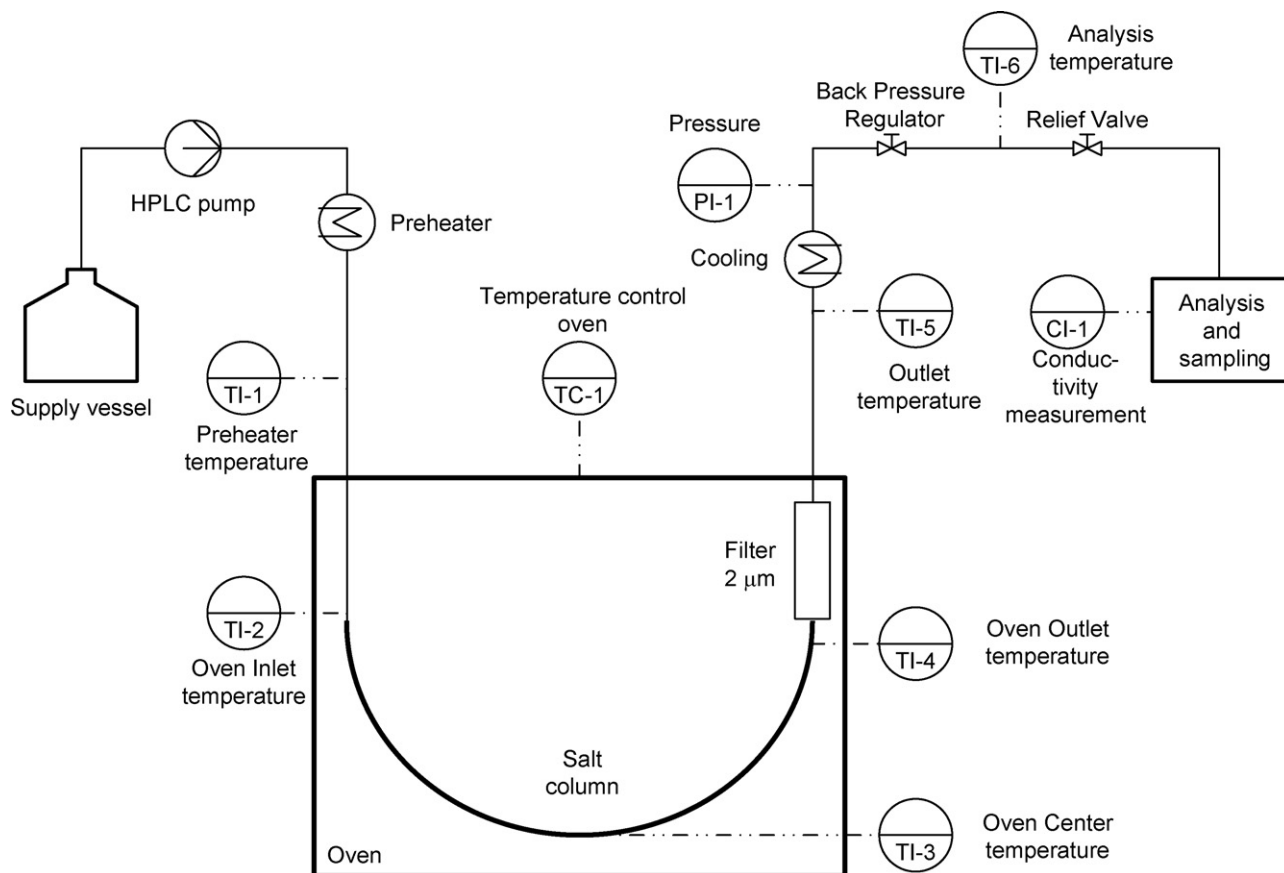


Fig. 3. Flow scheme of the experimental setup.

designed. The setup used is shown in Fig. 3. The operating range of the setup is up to 25 MPa as well as up to 723 K. The materials used in the heated parts of the setup were constructed from Hastelloy C for corrosion prevention and high-temperature strength (from TI-1 on till sampling) while the other parts were constructed of stainless steel or PEEK. In order to detect any amount of corrosion occurring, ICP analysis was performed on a frequent base for nickel, chrome, molybdenum and iron.

The essential part of the setup is a U-tube which is located inside a high-temperature oven. The inner diameter of the tube is 4.6 mm, the outer diameter 6.35 mm and the length 265 mm. Along the length of the column three thermocouples (PT100) are installed to measure the temperature profile at the inlet, center and outlet part. The heating of the oven consists of several electrical heating coils in the rear wall of the oven. To provide a large heat distribution area, two aluminum plates are placed behind and in front of the column and tightly connected to the column itself. The oven temperature is regulated via a Type K thermocouple which is located in direct vicinity of the front aluminum plate. To prevent any entrainment of particles and salt crystals outside the column, a filter with a 2 μ m Hastelloy filter is installed behind the column. The tubings connecting the U-tube with the rest of the setup have a diameter of 1/16 in.

In the experiments the feed solution is pressurized by using a high-pressure liquid chromatography pump (LabAlliance Series III) with a flow rate of 1–10 mL/min. The system pressure is regulated via a back pressure regulator (Tescom 26-1000 Series) while the system pressure is measured by a pressure sensor ranging from 0 to 40 MPa (Keller PA-23H). A second back pressure regulator (Tescom 44-2000 Series) is used to reduce the pressure to ambient since the lower limit of the first regulator is 1 MPa. Before the feed stream enters the oven, the stream is preheated via electrical heating (at TI-1) to guarantee a higher inlet temperature and resulting from that a constant temperature profile in the oven. After leaving the column, the stream is cooled down and depressurized before the stream is sampled and analysed. All process data is logged continuously for later interpretation of the results.

3.2. Analysis

The composition of the stream is analysed continuously via the measurement of the conductivity as well as batch-wise via sampling. The conductivity is measured contactless (Tracedec conductivity sensor). This method enables a direct analysis of the composition if a single salt is to be investigated yet it can be used during experiments with multiple salts present for a validation of an equilibrium state in the column.

The samples taken are analysed for all ions that can be present. The metal ion concentrations are analysed via an inductive coupled plasma atom emission spectrometer (ICP, PerkinElmer Optima 5300DV), while for the analysis of the present anions liquid chromatography is used (IC, Metrohm 741 Compact IC).

3.3. Modes of operation

Two different modes of operation are possible for the setup.

The first option is to pack a salt bed loosely in the U-tube. A pure deionized water stream is pumped through the column where the temperature and pressure of interest are established. The entering water stream gets saturated via the dissolution of the salt that is contained in the salt bed. The concentration of the outlet stream is the saturated equilibrium concentration of the system salt and water at the oven outlet temperature and the pressure in the column. Upon depletion of the salt bed the experiment has to be stopped and the column has to be filled again.

For this kind of operation mode it is assumed that the maximum solubility of the salt in the column is higher at higher molar densities. Resulting from that it is therefore impossible that precipitation of the salt occurs during the cooling and depressurization step and that the concentration in the sample taken corresponds to the one in the column. This method has been used for experiments with several salts (NaCl, Na₂SO₄) in supercritical water [45].

The second option is to use a feed stream with a known salt concentration. The U-tube is in this case either kept empty or filled with inert quartz beads. The temperature and pressure in the column are adjusted to the desired conditions. When the feed enters the column, the stream can be oversaturated regarding the conditions in the column and the salt used. If oversaturation occurs, the salt will precipitate till a phase equilibrium is reached. The resulting exiting stream is at its maximum saturation for the temperature and pressure in the column. The quartz beads are present in order to realize a higher crystallisation surface so that a kinetic limitation of the precipitation step can be neglected. A pressure drop along the column due to the bed can be neglected due to the low flow rate.

This method is preferable for salt systems with a low melting temperature in the range of the investigated temperatures like NaNO₃ [52]. The low melting point would otherwise lead to a possible clogging of the column and the filter by the melt. It also offers the opportunity to run experiments continuously without refilling the column and long downtimes. The column itself can be cleaned by rinsing it with pure deionized water. By this leakages in the system due to opening and closing the fittings can be minimized.

4. Results and discussions

4.1. Results of the comparison of (semi-)empirical approaches

In order to find a precise and efficient method to describe the solubility of salt molecules in SCW which can be used for design purposes and estimation calculations, three different approaches are compared: Eqs. (11) and (16) and the empiric approach Eq. (1). In all approaches the concentration will be described as the molality in mol/kg; the density of the pure solvent is the molar density in mol/L. The description of the concentration on a molality base is preferable due to the independence from the system parameters temperature and pressure. The usage of a molar density is more convenient since it allows an easier visualization of the molecules present per volume unit. The density of the pure solvent is calculated via the IAWPS95 equation of state [53].

As a first salt, sodium sulfate is investigated. Several sets of experimental data from literature covering a wide range of molar densities are used as a data base for the comparison [54,55,45,56,42,43]. As can be seen from Fig. 4 the three approaches have different degrees of agreement with the experimental data.³ The empirical approach is not capable of representing the experimental data over the whole range. Especially at lower molar densities deviations occur. This is related to the large differences in solubility of Na₂SO₄ over several orders of magnitude which cannot be represented by this simple approach.

The approaches Eqs. (11) and (16) are in good agreement with the experimental data. Nevertheless, exceeding the range of experimental data ($\rho < 8$ mol/L), one has to be aware that no experimental data is available. Resulting from that, these approaches should only be used in the range of $\rho > 8$ mol/L. For a better prediction over a greater range, additional measurements have to be

³ Enthalpy-Approach refers to Eq. (11), Cp-Approach to Eq. (16) and Empirical approach to Eq. (1).

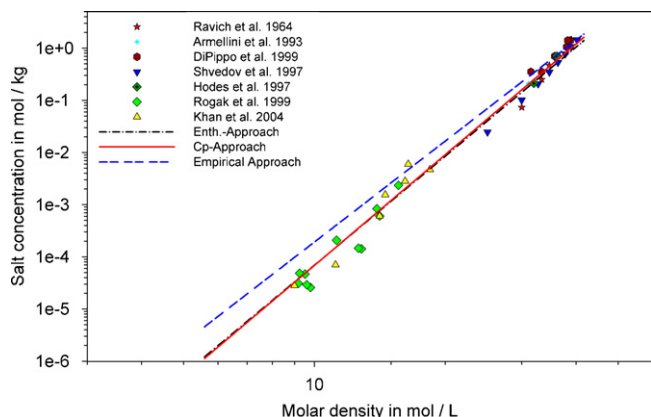


Fig. 4. Comparison of the approaches on the example of the solubility of Na_2SO_4 .

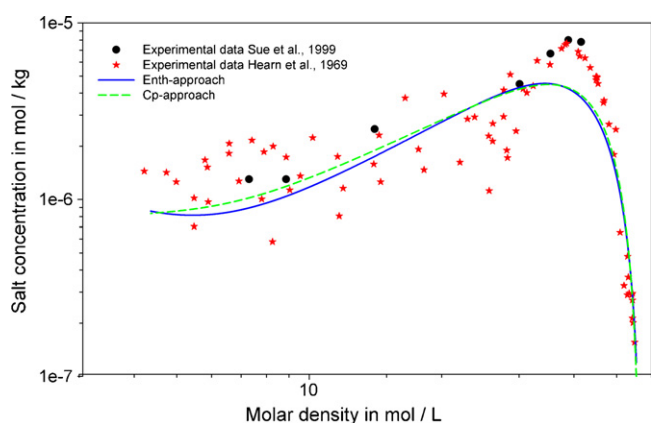


Fig. 5. Comparison of the approaches on the example of the solubility of CuO .

made. Still, both approaches are valid methods to describe the solubilities in the given range.

As further compounds PbO and CuO are investigated. Two sets of experimental data from literature [57,47] are used as a data base for the solubility of CuO , one [47] for PbO . As can be seen in Figs. 5 and 6, approach Eqs. (11) and (16) are in fair agreement with the experimental data. The large scattering in the experimental data of [57] at low densities results in less accuracy in the fitting procedure. Both approaches fail to reproduce the increased solubility of CuO in the range of 45–50 mol/L. Nevertheless, the general tendency of the solubility curve can be described as well as the accuracy of the

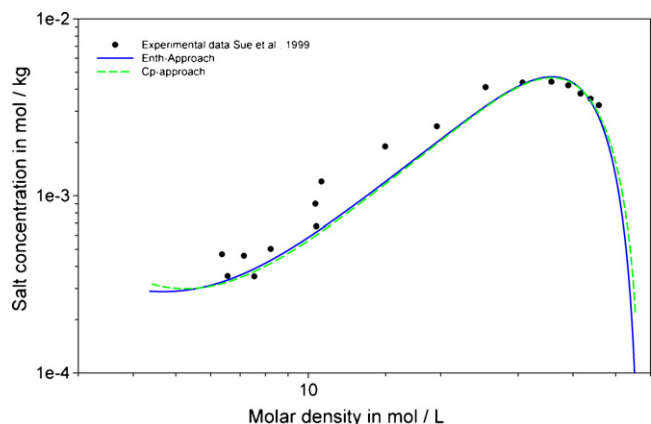


Fig. 6. Comparison of the approaches on the example of the solubility of PbO .

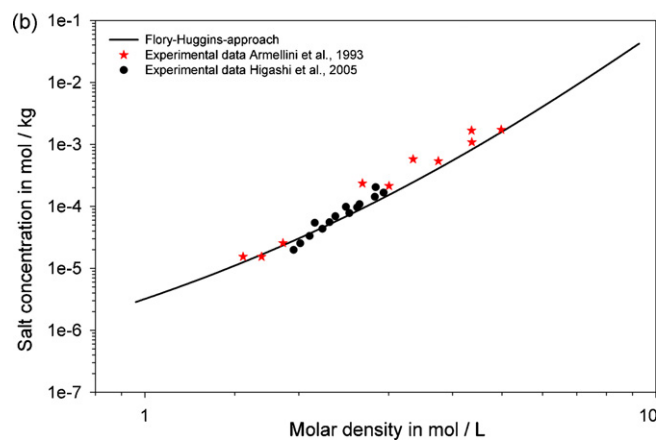
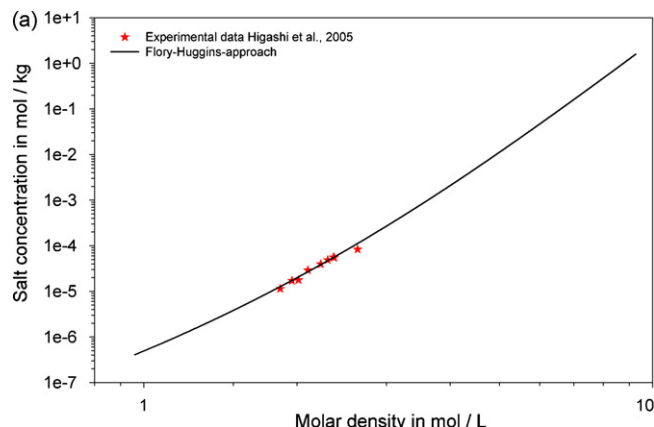


Fig. 7. Flory-Huggins-approach on KCl (a) and NaCl (b).

parameters used can be optimised by further experimental data. The description of PbO is good along the range of experimental data (cp. Fig. 6). The empirical approach is not capable of reproducing the experimental data and is not included in Figs. 5 and 6. The salts NaNO_3 and Na_2CO_3 as well as NaCl can also be described with good agreement with the mentioned approaches yet are not displayed here since no new conclusions can be made from their results.

In Fig. 7 the experimental data of KCl and NaCl is described with the Flory-Huggins approach using the experimental data of [49,50]. For both salts the agreement is good for the range of data available. The parameters used can be found in the papers mentioned above [49,50]. The experimental data was taken from [45,50].

When compared to the approaches Eqs. (16) and (11) (cp. Fig. 8), the Flory-Huggins approach does not substantially improve on the representation of the experimental data compared to the other two approaches. Nevertheless this approach is a valid method to be applied here; especially with regard to salt mixtures. Here the mixing rules for organic systems used with the Flory-Huggins approach could be adapted for systems which contain several salts.

4.1.1. Discussion of the results of the comparison

The empirical approach Eq. (1) is not capable to guarantee a good representation of experimental data.

The approaches Eqs. (11) and (16) are efficient and precise methods to describe the solubility of salts in supercritical water. Both are in good agreement with the experimental data presented.

To evaluate the quality of the proposed models, the correlation between the parameters can be considered as a significant factor. The correlation is an indication for the independence of the parameters from each other and thereby of the necessity of one parameter

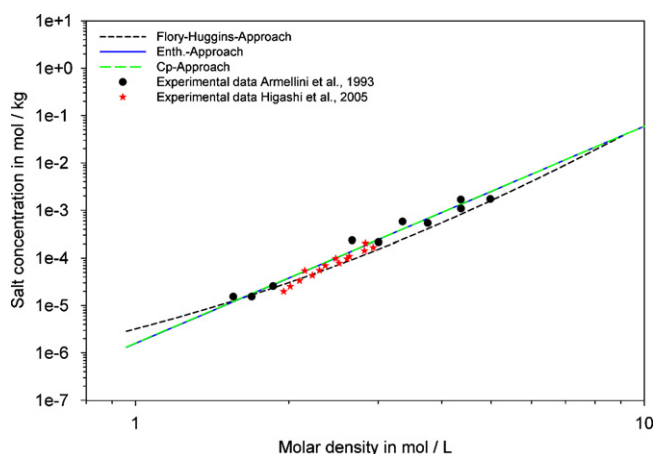


Fig. 8. Comparison of the approaches Eqs. (17), (16) and (11) on the example of NaCl.

[58]. Regarding the correlation coefficients between the parameters used in both approaches (cp. the correlation matrices of both approaches Fig. 9), it can be seen that there is a high degree of correlation between the parameters used in Eq. (16). The correlation coefficients between the parameters A' , B' and C' is almost unity resulting in a high degree of dependence of these parameters among each other. Concluding from that Eq. (16) has one parameter more than necessary. Compared to Eq. (11) no high degrees of

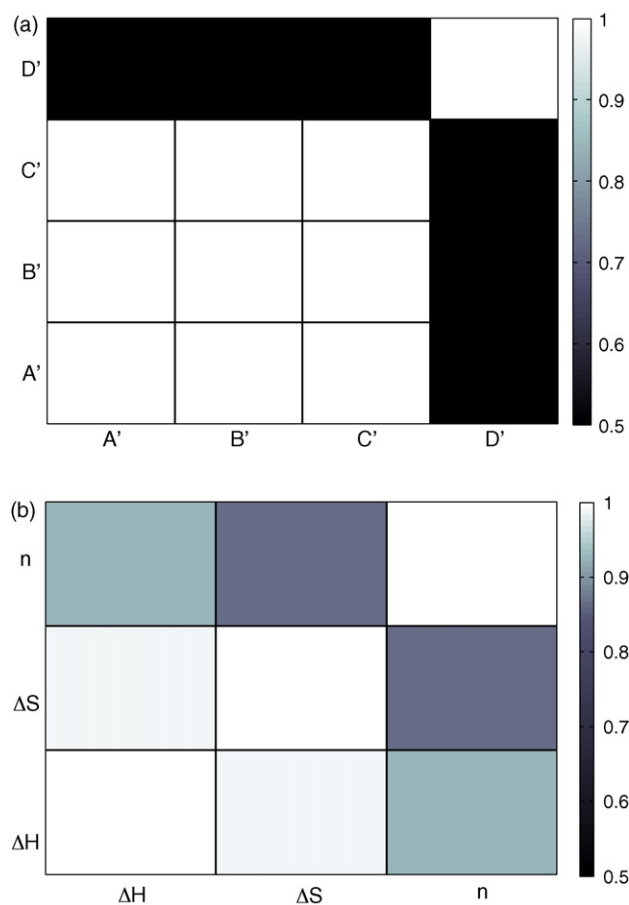


Fig. 9. Correlation diagram of the model parameters of Eq. (16)(a) and Eq. (11)(b) on the example of the solubility of Na_2SO_4 .

Table 1
Parameters for the approach Eq. (11)

Salt	ΔH (J/mol)	ΔS (J/mol K)	n (-)	References
NaCl	11,010	-92.76	3.99	[45] [50] [61]
NaNO_3	6,531	-78.6	3.06	[52]
Na_2SO_4	31,337	-166.61	7.132	[56] [55] [43] [42] [54] [45]
Na_2CO_3	-8,672	-132.14	3.52	[42]
CuO	23,750	-103.68	1.34	[47] [57]
PbO	27,901	-57.97	1.97	[47] [46]

correlation between the parameters appear here. The comparably high degree of correlation the parameters ΔS and ΔH results from the mathematical definition of the approach. Therefore it is advisable to use approach Eq. (11) for the calculation of solubilities of salt–water systems under supercritical conditions since the quality of both approaches is equal while Eq. (11) includes one parameter less.

Tables 1 and 2 contain the parameters for both approaches as well as the literature sources used for regression.

Due to the small number of salts investigated here, it is not possible to give a qualitative comparison of the parameters obtained for the various salts. Tendencies in the parameters are recognizable like the negative numbers in the entropy and the order of magnitude of the parameter n , yet further experimental data is needed. Relations between the ion properties as indicated in e.g. [52] are likely. Nevertheless, at the current state any predictive approach of the solubilities of salts in supercritical water is not possible due to the lack of experimental data.

4.1.2. Discussion of assumptions

One remark has to be made about the accuracy of the prediction of solubilities outside the range of experimental data available. Although general tendencies can be described one has to be careful about the results at high and low densities where no or only little data is available. Especially the effect of high temperatures far beyond the given validity range leads to growing errors in the estimation.

Additionally, the hydration number n is not expected to be an integer since the solvation complexes are regarded in these approaches as metastable complexes with a changing number of

Table 2
Parameters for the approach Eq. (16)

Salt	A' (-)	B' (-)	C' (-)	D' (-)	References
NaCl	-59.93	-2513.7	6.23	4.01	[45] [50] [61]
NaNO_3	-18.04	-60.99	1.13	3.06	[52]
Na_2SO_4	-339.43	-21,086	43.155	7.6579	[56] [55] [43] [42] [54] [45]
Na_2CO_3	-1.8	-57.45	-1.927	3.49	[42]
CuO	28.38	5425.9	-5.57	1.09	[47] [57]
PbO	-33.12	1258.9	3.52	2.01	[47] [46]

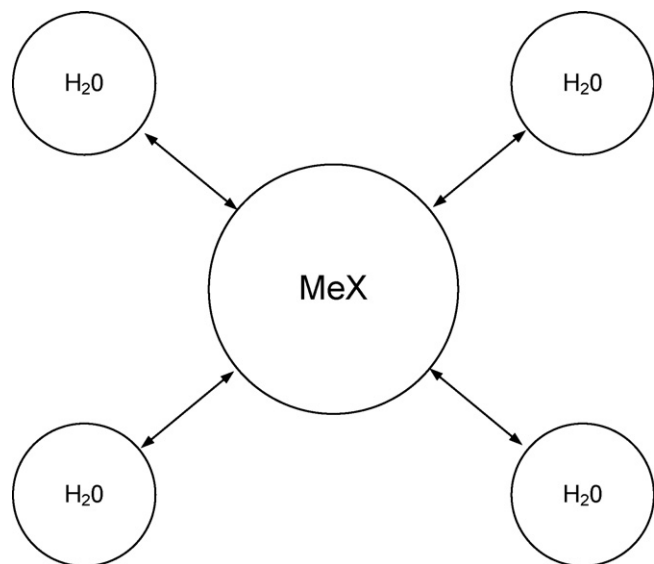


Fig. 10. Changing hydration structure of a salt molecule in SCW.

water molecules included (see Fig. 10). Regarding this fact the hydration number has to be considered as an *average equilibrium association number* [44]. To obtain a more sophisticated determination of the hydration number, it might be advisable to develop an expression including parameters describing the solvation parameters as a function of the system parameters temperature and pressure. Here the usage of the dielectrical constant or the description of the hydration sphere and its properties via Stokes radii or variation of the mean spherical approach are possible approaches.

Another issue is the degree of association of the salts in supercritical water. In the approximations mentioned above it is assumed that all salts are completely associated and that neither chlorine ions nor sodium ions are present. For NaCl, several papers indicate that there is still a small amount of dissociated ions of sodium chloride present in supercritical water which is not taken into consideration in the approaches [33,59]. In Fig. 11 the amount of associated sodium chloride and the amount of dissociated sodium chloride is shown. The concentration of the associated sodium chloride c_{NaCl} is calculated by the results presented above at a given temperature and pressure. The concentrations of the associated and dissociated ions is calculated via the association equilibrium using

the equilibrium data of [60].

$$K_a \approx \frac{c_{\text{NaCl}}}{c_{\text{Na}^+} \cdot c_{\text{Cl}^-}} \quad (18)$$

$$\approx \frac{c_{\text{NaCl}}}{c_{\text{Na}^+}^2} \quad (19)$$

$$\Rightarrow c_{\text{Na}^+} \approx \sqrt{\frac{c_{\text{NaCl}}}{K_a}} \quad (20)$$

Resulting from the small amount of dissociated ions present in the system, a total association of sodium chloride can be assumed without further complications.

Also the presence of side reactions, i.e. the hydrolysis of NaCl in supercritical water or the shift from Na_2CO_3 to NaHCO_3 is neglected and not taken into consideration [45,61].

Using the density of the pure solvent and neglecting activity coefficients for all species is a straightforward yet efficient simplification of the simple systems investigated here. Nevertheless, it is doubtful if these assumptions are still valid for more complex systems (e.g. mixtures) since interactions are to be expected, especially if still ions are present in the system due to incomplete association.

4.2. Experimental results

Since NaCl is the major component of most of the common salt–water systems in nature and industry, the system NaCl– H_2O is chosen as a reference system. To extend the available solubility data and to validate the applicability of the current experimental setup and methods on the qualitative analysis of solubilities in supercritical water, NaCl was investigated in a range of 170–240 bar and 370–410 °C.

For the experiments a feed stream with a known concentration and an empty column were used. To avoid unnecessary amounts of precipitated salts, the inlet concentration was adjusted to the molar densities investigated. For lower densities ($\rho < 6$ mol/L) a solution of 0.025 mol NaCl, for medium densities ($6 < \rho < 9$ mol/L) of 0.04 mol NaCl and for higher densities ($\rho > 9$ mol/L) of 0.075 mol NaCl was used. The volume flow for all experiments was set to 1 mL/min which results in a residence time of the solution in the column of appr. 260 s. During the experiments, the conductivity of the outlet stream is measured continuously. If the conductivity signal is constant for a longer period ($t \geq 10$ min), it is assumed that an equilibrium state is reached inside the column and that the outlet concentration corresponds to the equilibrium concentration. Per equilibrium state in the column two samples were taken in an interval of 30 min and analysed via IC and ICP. For the calculation of the density in the column the outlet temperature of the column (TI-4) and the pressure of the pressure sensor (PI-1) were used. A pressure drop along the tubing from the outlet of the column and the pressure sensor can be neglected due to the low flow velocities. The temperature and pressure variation recorded during an experiment is shown in Fig. 12. The maximum deviation in pressure during all experiments was ± 0.2 MPa; the maximum deviation in temperature ± 0.8 K.

For most of the experiments no severe difference between the measured sodium and the measured chlorine concentration was observed. This would have indicated the occurrence of hydrolysis of NaCl. This is supposed to be related to the higher densities/lower temperatures investigated than in comparison to the work of Armellini and Tester [45], where hydrolysis occurred at temperatures higher than 450 °C and pressures of 150 bar and lower. Nevertheless, only the sodium concentrations were used for further evaluation to have conformity with previous works on NaCl [45,50].

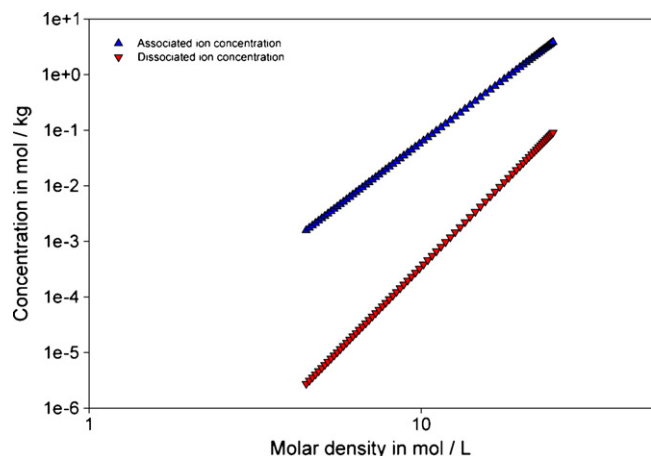


Fig. 11. Association of NaCl in supercritical water and the solubility of NaCl [60].

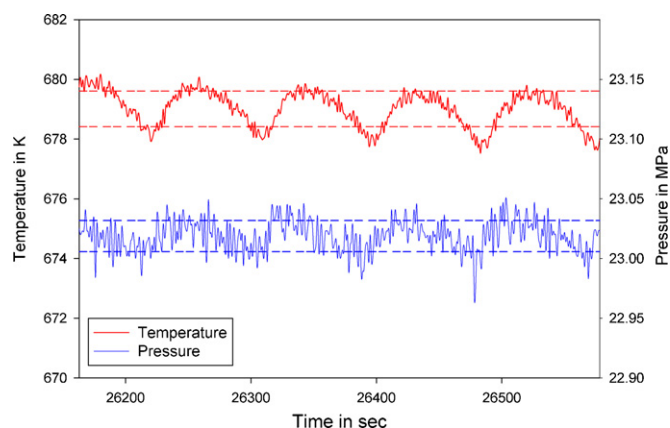


Fig. 12. Example for the temperature and pressure behavior during an usual experiment. Dashed lines represent the standard deviations.

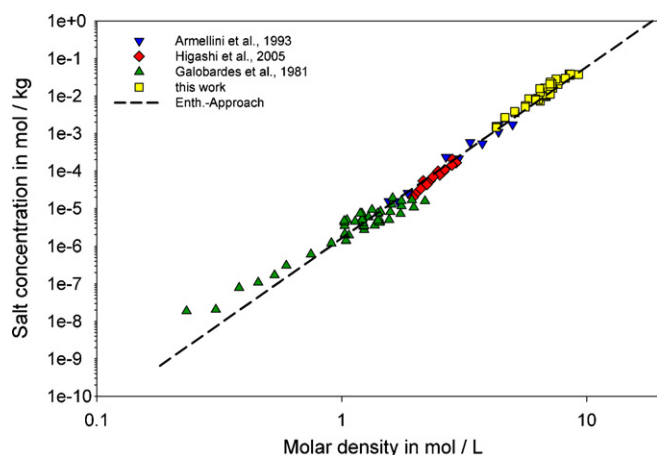


Fig. 13. Comparison of experimental NaCl solubility results and approach predictions.

Table 3

New parameters for the approach Eq. (11) including the experimental data of this work

Salt	ΔH (J/mol)	ΔS (J/mol K)	n (–)	References
NaCl	11010	–94.56	4.569	[45] [61] [50] This work

Fig. 13 shows a comparison of the solubility data available from literature for NaCl and the experimental results obtained from the present study. The experimental results presented in this work cover a density range higher than in previous works ($4 < \rho < 10$ mol/L). As can be seen from Fig. 13, the experimental data is in good agreement with the trend of the other data sets. The parameters acquired using the new experimental data for the regression of Eq. (11) as well as the old data sets can be found in Table 3.

Table A.1 in Appendix A contains the results of our experiments used for Fig. 13 and the regression.

5. Conclusions

In this work three (semi-)empirical approaches have been applied to describe the solubility of inorganic compounds in

supercritical water. These approaches have been correlated to experimental data available in open literature. The assumptions for all three approaches and possible error sources were critically reviewed. One approach (Eq. (11)) has been selected as the most suitable one due to its quality of fit and its simple yet efficient structure. Parameters for this approach for the salts NaCl, NaNO₃, Na₂CO₃, Na₂SO₄, PbO and CuO have been presented.

An experimental setup for the measurement of solubilities has been presented as well as the experimental procedure. New solubility data for NaCl in the range of 380–410 °C and 170–235 bar has been shown and correlated with the chosen approach. The presented experimental data were consistent with existing literature data yet extended the investigated range to higher densities. In order to compare the quality of empirical approaches and of an EOS for the current purpose, it is of interest to correlate the available literature data also with an EOS. Also the application of Eq. (11) to already available or new experimental data appears to be an interesting subject.

Appendix A. Experimental results

See Table A.1.

Table A.1

Experimental results

Temperature (K)	Pressure (MPa)	Molar density (mol/L)	Concentration Na (mmol/L)
654.1 ± 0.5	22.5 ± 0.02	9.84	87.00
656.2 ± 0.5	22.3 ± 0.02	8.90	48.68
666.8 ± 0.8	23.5 ± 0.02	8.60	38.26
657.1 ± 0.4	22.2 ± 0.02	8.47	35.64
666.3 ± 0.5	23.1 ± 0.03	8.18	38.60
656.7 ± 0.4	21.7 ± 0.02	7.95	29.85
672.6 ± 0.6	23.3 ± 0.02	7.68	28.39
673.3 ± 0.6	23.3 ± 0.01	7.63	25.28
673.2 ± 0.6	23.1 ± 0.24	7.49	20.37
675.5 ± 0.6	23.0 ± 0.01	7.26	16.01
672.0 ± 0.5	22.6 ± 0.01	7.21	21.39
673.4 ± 0.6	22.6 ± 0.01	7.12	15.91
674.3 ± 0.6	22.7 ± 0.01	7.10	23.48
674.8 ± 0.5	22.7 ± 0.02	7.10	11.14
675.2 ± 0.7	22.7 ± 0.01	7.07	20.93
679.0 ± 0.6	23.0 ± 0.01	7.01	12.61
679.1 ± 0.6	23.0 ± 0.02	7.00	12.58
676.2 ± 0.6	22.5 ± 0.02	6.86	10.88
683.8 ± 0.6	23.2 ± 0.02	6.84	10.23
676.6 ± 0.6	22.5 ± 0.02	6.83	9.65
684.6 ± 0.6	23.2 ± 0.02	6.78	9.61
678.4 ± 0.6	22.5 ± 0.02	6.74	15.35
678.7 ± 0.6	22.6 ± 0.02	6.73	16.39
667.1 ± 0.5	21.0 ± 0.02	6.46	12.66
681.6 ± 0.7	22.4 ± 0.02	6.46	7.32
667.7 ± 0.5	21.0 ± 0.02	6.43	15.67
684.0 ± 0.6	22.4 ± 0.01	6.35	7.96
682.7 ± 0.6	22.3 ± 0.02	6.35	8.16
683.2 ± 0.6	22.3 ± 0.02	6.32	8.70
671.9 ± 0.7	21.0 ± 0.02	6.19	7.88
672.1 ± 0.7	21.0 ± 0.02	6.18	8.44
674.9 ± 0.6	20.6 ± 0.02	5.80	8.40
673.0 ± 0.6	20.1 ± 0.02	5.62	5.53
673.0 ± 0.6	20.1 ± 0.02	5.61	5.05
673.3 ± 0.6	19.0 ± 0.02	5.10	3.59
673.6 ± 0.6	19.0 ± 0.02	5.09	3.89
673.4 ± 0.6	18.0 ± 0.02	4.64	2.68
673.4 ± 0.6	18.0 ± 0.02	4.63	2.60
673.3 ± 0.7	17.1 ± 0.01	4.28	1.44
673.7 ± 0.6	17.1 ± 0.01	4.27	1.53

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